

Photophysical parameters of pyrazolylbenzimidazole dyes : possible laser media

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Abstract : The various molecular parameters of singlet states of some newly synthesized dyes belonging to pyrazolylbenzimidazole group have been determined from their absorption and fluorescence spectra. Evaluation of these parameters in the light of their suitability as laser dyes and comparison with the general lasing criteria showed that they are good candidates for laser media. The sensitized fluorescence study suggested that the dyes are suitable for energy transfer dye mixture dye lasers.

Keywords : Absorption and emission cross section, optical gain, dye Lasers

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1. Introduction

Organic dyes are wide band absorbers and emitters of UV and visible radiation. They have become extensively useful in dye lasers in view of their wide range of tunability. There is a growing activity in the search of new dyes for dye lasers [1-3]. Keeping in view, the structure of known lasing dyes, some new dyes belonging to pyrazolylbenzimidazole group have been synthesized [4]. We have made an attempt to characterize these dyes with the photophysical parameters. These molecular parameters have been evaluated to find their suitability as laser media. Further, the study of sensitized fluorescence showed that these dyes are suitable for energy transfer to improve dye laser performance.

2. Molecular structure, spectra and photophysical parameters

The molecular structure of the new dyes (I-V) is shown in Figure 1. The absorption spectra of benzimidazole derivatives recorded at low concentration (1×10^{-5} M Litre⁻¹) in dioxane show different absorption bands in the UV region extending to visible region with peak absorption at different wavelengths (Table 1).

The molar extinction co-efficient (ϵ) which is a measure of the ability to absorb light determines the penetration depth of pump radiation in the solution and in turn provides photon flux needed to pump the dye molecules to S_1 state for laser action. This determines

Dye	Structure	Name
I		2-(1-Phenyl-5-p-chlorophenyl-4,5-dihydro-4-hydroxy-3-pyrazolyl) benzimidazole
II		1-Methyl-2-(1-phenyl-5-p-chlorophenyl-4,5-dihydro-4-hydroxy-3-pyrazolyl) benzimidazole.
III		1-Benzyl-2-(1-phenyl-5-p-chlorophenyl-4,5-dihydro-4-hydroxy-3-pyrazolyl) benzimidazole.
IV		2-(1-Phenyl-5-phenyl-4,5-dihydro-4-hydroxy-3-pyrazolyl) benzimidazole.
V		1-Benzyl-2-p-methoxycinnamoyl benzimidazole.

Figure 1. Molecular structure of the dyes.

the threshold pump power. The values of ϵ were obtained from the optical density profile of the dye solution [5]. The absorption interaction cross section (σ_a) is a quantity associated with extinction co-efficient and is a measure of the probability for the occurrence of absorption. The absorption interaction cross sections were determined for these dyes using ϵ values [6],

$$\sigma_a (\lambda) = \frac{2.303 \times 1000 \epsilon (\lambda)}{N} \quad (1)$$

where N is the Avogadro's number.

It is a constant quantity of the dye at the absorbing wavelength. These dyes were found to have high values of ground state absorption cross section around 330 nm, most suitable for N_2 laser (337.1 nm) pumping.

Table 1. Singlet-Singlet absorption and emission characteristics of dyes.

Dye	Absorption range (peak, λ_a) (nm)	Extinction coefficient at λ_a ϵ_m (LM ⁻¹ cm ⁻¹)	Absorption cross section at 337.1 nm $\sigma_{01} \times 10^{16}$ (cm ²)	Fluorescence range (peak, λ_f) (nm)	τ_f (ns)	Q_f	Gain G (dB/cm)
I	317-432 (374)	68600	0.96	395-595 (452)	3.92	0.49	220
	264-317 (291)	16800	—				
	224-264 (238)	29300	—				
	210-224 (215)	22600	—				
	318-424 (376)	26100	0.33	392-605 (452)	4.24	0.74	208
	284-318 (308)	4900	—				
	325-431 (378)	34700	0.50	397-605 (455)	3.95	0.65	235
III	216-325 (236)	41800	—				
IV	314-432 (375)	92700	1.22	420-555 (480)			
V	280-460 (370)	43500	1.04	435-548 (474)			
C 2	270-425 (364)	54300	0.30	380-525 (432)	3.61	0.77	286

Another parameter used in dealing with the probability of an electronic transition is the oscillator strength (f). The oscillator strength is related to the experimental extinction coefficient and is determined from the relation [7],

$$f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu, \quad (2)$$

where the integration is carried over the absorption band.

The fluorescenc spectrum of the new dyes covers the entire visible range and has no structure. A parameter of significance for laser medium that determines the efficiency of the laser is the fluorescence quantum yield (Q_f). It is an indirect measure of non-radiative transitions that compete with the emission of light. The high values of quantum yield minimise the probability of $S_1 - S_2, S_3 \dots$ higher singlet states (excited state absorption), $S_1 - S_0$ (internal conversion), and $S_1 - T_1$ intersystem crossing [2, 8]. Quantum yield is related to the experimental parameters [9],

$$Q_f(x) = Q_f(r) \frac{A(r)}{A(x)} \left[\frac{n(x)}{n(r)} \right]^2 \frac{S(X)}{S(r)} \quad (3)$$

where A is the optical density at the excitation wavelength; S denotes the area under the corrected fluorescence curves and X and r refer to the unknown and reference samples, respectively. The values of quantum yields of benzimidazole dyes have been determined with respect to a standard dye, Coumarin 2.

For laser action to occur, the singlet state lifetime should be short. The fluorescence lifetime of the dyes I, II, III were determined from the decay curves recorded using Edinburgh's time correlated single photon counting (TCSPC) fluorimeter (Model-199) and were found to be in the nanosecond range (Table 1). Figure 2 represents the nature of the decay curve of the dyes under study and is well fitted to a single exponential function. The Chi-square values varied from 1.2 to 1.8 for the various curves recorded.

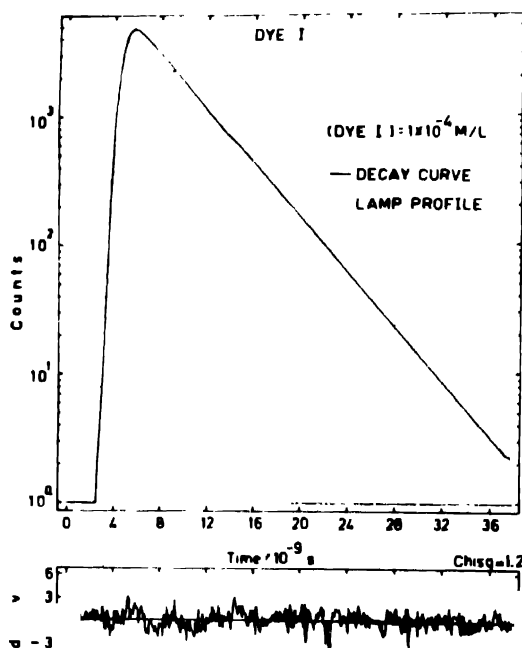


Figure 2. Fluorescence decay curve.

The stimulated emission cross section (σ_e) and gain (G) of an optical medium are important molecular parameters which throw light in assessing the ability of the dye medium to lase. The values of σ_e for $S_1 - S_0$ transition were computed from the relation [10],

$$\sigma_e(\lambda) = \frac{\lambda^4 F(\lambda)}{8\pi c n^2 \tau_r \int F(\lambda) d\lambda} \quad (4)$$

where the integration is carried over the fluorescence band.

Gain provides information about excited state population and is related to molecular parameters. The single pass gain was calculated for a dye solution of concentration $N(\text{cm}^{-3})$ for an optical pumping using the expression [11],

$$G(\lambda) = 10 \log \{ \exp(-g(\lambda)L) \} \quad (5)$$

$$\text{where, } g(\lambda) = -N_0\sigma_a(\lambda) + N_1\sigma_e(\lambda), \quad (6)$$

L is the Cuvette length; N_0, N_1 refer to populations of S_0 and S_1 states and σ_a, σ_e denote the absorption and emission cross sections respectively.

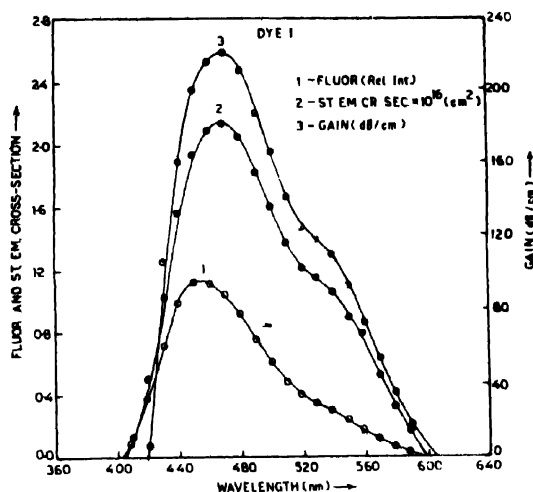


Figure 3. Variation of stimulated emission cross section and gain over the fluorescence region.

The variation of $\sigma_e(\lambda)$ and $G(\lambda)$ along the fluorescence band are shown in Figure 3 for dye I as a representative. The stimulated emission cross section profile follows the

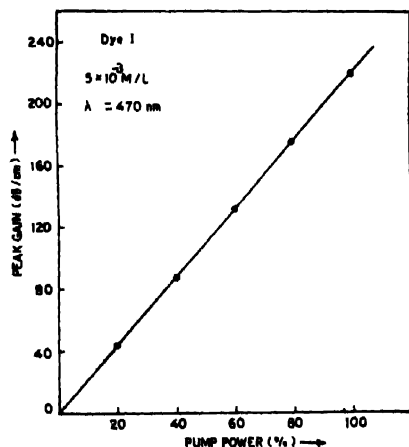


Figure 4. Gain as a function of pump power.

fluorescence spectrum with a shift in the peak towards the longer wavelength side but the gain is maximum at the peak wavelength of the stimulated emission cross section indicating the possible lasing peak and turning range. The gain measured with different pump powers is linear (Figure 4) and passes through the origin indicating that the ground state reabsorption loss is not present [12].

The fluorescence spectra of the new dyes were enhanced in the presence of 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD) and 2-(4-biphenyl)-5-(*p*-tert-butylphenyl)-1,3,4-oxadiazole (BPBD) due to excitation energy transfer in the mixture of dyes. Energy transfer studies using PBD and BPBD with new dyes as donor and acceptor pairs were made by recording the fluorescence spectra at different acceptor concentrations (Figure 5).

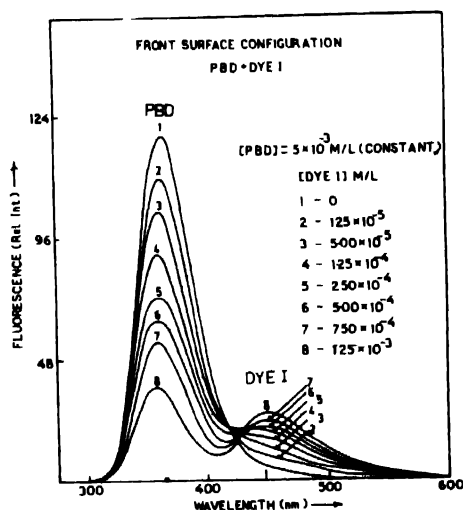


Figure 5. Fluorescence spectra of PBD and Dye I in mixture.

The energy transfer rate parameters determined from the fluorescence intensity measurements for all the dye mixtures are of the order of $10^{12} \text{ LM}^{-1} \text{ S}^{-1}$. High transfer rates show that there is a considerable excitation energy transfer from donor to acceptor indicating good combination of these dyes for dye mixture laser.

When we consider various molecular parameters of these dyes we find that they compare very well with the corresponding values of the standard laser dye C 2. Evaluation of these values shows (Table 2) that they fulfil the two general lasing criteria; (i) $\sigma_{e, \text{max}} \geq 0.5 \times 10^{-16} \text{ cm}^2$ and (ii) $f \geq 10^{-4} \Delta \nu$ ($\Delta \nu$ – FWHM of fluorescence spectrum), proposed by Maier *et al* [13], after testing a large number of organic laser dyes. Another requirement of short radiative lifetime (*ns* range) suggested by Shank [14] is also satisfied by these dyes. Fulfilment of these necessary conditions indicates that they have high potential for lasing and suggests that they are good candidates for laser active medium.

Table 2. Oscillator strength and emission cross section values for lasing criteria.

Dye	f	$10^{-4} \Delta\nu$	$\sigma_{e, max} \times 10^{16}$ (cm^2)
I	1.36	0.42	2.14
II	0.42	0.43	0.83
III	0.57	0.43	0.80
C 2	1.01	0.44	2.14

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